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THE OXIDATION OF 2, 4, 6 TRI-ODE PHENOL

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BY

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[Contribution from the School of Chemistry of the University of Minnesota]

The Oxidation of Sym-Triiodophenol[1]

By W. H. Hunter and Mary L. Morse

The present research upon the oxidation of *sym*-triiodophenol was undertaken for the purpose of ascertaining further facts concerning the nature and relative stability of triiodo Type A and diiodo Type B radicals.

A preliminary qualitative survey was made of the oxidation of *sym*-triiodophenol in non-aqueous or in aqueous media by several oxidizing agents.

The oxidation of *sym*-triiodophenol in alkaline solution by potassium ferricyanide was then chosen for further study. The products of this reaction were a large quantity of Lautemann's Red, a small quantity of the dinuclear quinone, 2,6,2′,6′-tetraiododiphenoquinone,[2] and an unstable compound which was not isolated. No phenoxyquinones were found.

Experiments were also carried out for the purpose of showing the relative oxidizing power of the crude oxidation products obtained from the respective oxidations of *sym*-trichloro-, tribromo-, and triiodophenols in glacial acetic acid by a large excess of chromium trioxide. The crude oxidation from the trichlorophenol showed the presence of about 97% of the mononuclear dichloroquinone, which has long been known to be the chief oxidation product formed under these conditions, whereas the crude

(1) The work described in this paper formed a part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Mary L. Morse in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1929. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. Smith.

(2) Kammerer and Benzinger [*Ber.*, **11**, 557 (1878)] assigned this formula to a substance which they obtained by the action of potassium tri-iodide solution on a boiling solution of phenol in sodium carbonate. However, the work of Hunter and Woollett indicated that the material obtained by Kammerer and Benzinger was Lautemann's Red. In this case, 2,6,2′,6′-tetraiododiphenoquinone is a new compound.

oxidation product of triiodophenol showed the presence of only 86% of mononuclear diiodoquinone. The crude oxidation product of tribromophenol, with 74% of mononuclear dibromoquinone, proved to be more similar to the oxidation product of triiodophenol than to that of the trichlorophenol.

The results of this research upon the oxidation of *sym*-triiodophenol indicate a pronounced tendency toward the rapid formation of Type B radicals, when this compound is treated with reagents capable of disengaging the hydrogen of the phenolic hydroxyl group. Since no phenoxyquinones were isolated, it is assumed that an iodinated Type A radical is very much less stable than its trichloro and tribromodimethoxy analogs. On the other hand, a comparison of the relative oxidizing power of the crude oxidation products of *sym*-trichloro, tribromo and triiodophenols indicates that polymerization of Type B radicals, proceeding concurrently with oxidation, is a more pronounced property of diiodo Type B radicals than of dichloro Type B radicals.

Another characteristic of the diiodo Type B radical is brought out by a comparison of certain of the products isolated in this study, with the oxidation products of pyrogallol dimethyl ether, as reported by Graebe and Hess,[3] and of tribromoresorcinol studied by Davis and Hill.[4] All of these products may be considered to be derivable from the polymerization of Type B radicals, although it is noteworthy that the mode of polymerization is apparently capable of variation, for from the diiodo Type B radicals there result both carbon to carbon and carbon to oxygen ties, the latter type predominating, whereas the dimethoxy Type B radical and the dibromoreso Type B radical exhibit a carbon to carbon type of polymerization.

No compounds ascribable to a carbon to carbon polymerization of Type B radicals were isolated in the work of Hunter and Levine[5] on the oxidation of tribromopyrogallol dimethyl ether, or in that of Hunter and Minerva Morse[6] on the oxidation of *sym*-trichlorophenol. All of the compounds isolated in these investigations must be looked upon as resulting from the carbon to oxygen type of polymerization.

The variation in the mode of polymerization evidenced by the types of polymers described above may be considered as due in part at least to the character of the Type B radicals involved. Thus, if a Type B radical of a given kind were more stable in a benzenoid than in a quinoid form, the corresponding polymer would be of the carbon–oxygen type, whereas if a Type B radical existed predominantly in the quinoid form, the carbon–carbon type of polymerization would occur.

(3) Graebe and Hess, *Ann.*, **340**, 232 (1905).
(4) Davis and Hill, THIS JOURNAL, **51**, 500 (1929).
(5) Hunter and Levine, *ibid.*, **48**, 1608 (1926).
(6) Hunter and Morse, *ibid.*, **48**, 1615 (1926).

The results of this investigation indicate that: (1) if the triiodo Type A radical is capable of existence, it is less stable than the Type A radicals previously studied in this Laboratory; (2) the diiodo Type B radical, on the other hand, is more stable and exhibits a greater tendency toward polymerization than its dichloro analog; (3) diiodo Type B radicals are capable of polymerizing both carbon–carbon and carbon–oxygen, the latter representing the predominating tendency.

Experimental Part

The Effect of Various Oxidizing Agents on Sym-Triiodophenol.—The attempted oxidation of triiodophenol in glacial acetic acid by sodium nitrite resulted in the replacement of one of the iodine atoms by a nitro group. Nitro compounds of this type also resulted from the reaction between triiodophenol in carbon tetrachloride and nitrogen trioxide. No oxidation products were isolated in either case. The results of this investigation were in agreement with those reported earlier by Raiford and Heyl.[7]

In the oxidation of triiodophenol in benzene by lead dioxide a buff colored amorphous material, presumably polydihalogenophenylene oxide resulting from the catalytic decomposition of the salts of *sym*-triiodophenol, was the only product formed in appreciable amount. About 50% of the triiodophenol was recovered unchanged after a twenty-four hour reaction period. This reaction was not studied further.

The oxidation of triiodophenol in glacial acetic acid by chromium trioxide resulted in the formation of a large quantity of *m*-diiodo-*p*-quinone, some amorphous material and a small quantity of tetraiododiphenoquinone.

Triiodophenol was oxidized in neutral solution by potassium permanganate. The chief product of this reaction was a reddish amorphous mixture. This was reduced by treatment with sulfur dioxide, and extracted with acetone. The insoluble amorphous material amounted to about 75% of the theoretical yield calculated on the basis of the exclusive formation of the Type B radical. This material was probably the amorphous oxide. It was not investigated further. The acetone extract was evaporated to a small volume. A gum-like material was left which was purified by repeated crystallizations from ethyl acetate. The crystalline product melted at 260–263°, although some decomposition and evolution of iodine were noticeable at around 245°. This compound was found to be identical with the 2,6,2′,6′-tetraiododiphenol to be described below.

Anal. Calcd. for $C_{12}H_6O_2I_4$: I, 73.62. Found: (Carius) I, 73.56, 73.52.

Oxidation of Sym-Triiodophenol in Alkaline Solution by Potassium Ferricyanide

Preparation of the Oxidation Product or "Red Mixture."—A solution of 70 g. (10 equivalents) of potassium ferricyanide in 300 cc. of water was added in one lot with stirring to a solution of 10.00 g. (1 equivalent) of *sym*-triiodophenol dissolved in 15 cc. of 2 *N* potassium hydroxide (1.5 equivalents) and 200 cc. of water. A heavy reddish brown precipitate appeared immediately. The mixture was filtered, and the residue washed thoroughly with water. The filtrate contained some iodine but no organic material.

The precipitate, which will be called the "red mixture," was dried to constant weight at 60°. The average weight of the product at this point (for several runs) was 7.56 g. The theoretical weight calculated on the basis of the exclusive formation of Type B radicals, and the compounds which might result from subsequent polymerization of these, was 7.29 g.

Reduction of the "Red Mixture" and Isolation of 2,6,2′,6′-Tetraiododiphenol.—Ten lots of "red mixture" prepared as described above were combined while still moist

(7) Raiford and Heyl, *Am. Chem. J.*, **43**, 393 (1910); **44**, 209 (1910).

and suspended in a liter of water. A solution of 14.4 g. of hydrazine sulfate in 400 cc. of 2 *N* potassium hydroxide was added to this suspension and the mixture was placed on a steam-bath. After thirty to forty minutes the solution was decanted from the residue and the latter was thoroughly extracted with warm 1 *N* potassium hydroxide. The filtrate and washings were combined and acidified with acetic acid. A white precipitate was formed, which amounted to 4.3 g. or 5.6% yield of alkali soluble product.

This material was difficultly soluble in most organic solvents, but was purified by several crystallizations from ethyl acetate. It melted at 260–265° with noticeable decomposition at 245°. A molecular weight determination was impossible due to insolubility of the substance.

Anal. Calcd. for $C_{12}H_6O_2I_4$: I, 73.62. Found: (Carius) I, 73.64, 73.50.

2,6,2′,6′-Tetraiododiphenoquinone.—Two hundred cc. of a saturated solution of 2,6,2′,6′-tetraiododiphenol in glacial acetic acid was treated with 0.5 g. (50 equivalents) of chromium trioxide in 1 cc. of water and 25 cc. of glacial acetic acid. A drop of concentrated sulfuric acid was added to the mixture which was stirred for five minutes and filtered; 0.12 g. of a dark green crystalline product was obtained. The mother liquor was diluted with water but no further precipitation occurred. The crystalline product could not be purified further, due to its insolubility. It did not melt.

Anal. Calcd. for $C_{12}H_4O_2I_4$: I, 73.82. Found: (Carius) I, 73.09, 73.13.

Anal. (Hydrazine method for quinoid oxygen). Calcd. for $C_{12}H_4O_2I_4$: O, 4.65. Found: O, 4.66, 4.58.

Evidence for the Presence of an Unstable Compound in "Red Mixture."—A sample of freshly prepared "red mixture" was extracted with dry ether and filtered rapidly. The residue, a clean, red powder, was extracted with dry benzene, yielding a deep red solution. Gradual evaporation of the solvent at room temperature and atmospheric pressure gave deep red crystals, with a gold sheen. This substance decomposed without melting, and all attempts to purify it by recrystallization failed as the dry material changed rapidly to a reddish brown amorphous powder. A solution of the red crystals left a varnish-like deposit upon evaporation of the solvent, and no crystalline material could be obtained after this change had occurred. Several attempts were made to determine the quinoid oxygen content of this substance. The results were variable, but the highest value obtained was roughly 5.4%. The calculated quinoid oxygen content of tetraiododiphenoquinone is 4.65%, of *m*-diiodo-*p*-quinone, 8.88%, and of the as yet unknown triiodophenol iodide, 5.38%.

Comparison of the Quinoid Oxygen Content of the Crude Oxidation Products of Sym-Trichloro, Tribromo and Triiodophenols

Preparation of the Oxidation Product of the Sym-Trihalogenated Phenol.—1.00 gram of the *sym*-trihalogenated phenol was dissolved in a small quantity of glacial acetic acid at 50°. A solution of 19 equivalents of chromium trioxide in an equal weight of water was added to this solution all at once. After a few seconds (5–10 in the case of the trichlorophenol, 20 in the other two cases) the mixture was poured with

TABLE I

CRUDE OXIDATION PRODUCTS

Halogenated phenol, *sym*-tri-	Chloro	Bromo	Iodo
Crude oxidation product, g.	0.40	0.35	0.66
Yield, %	45.2	44.2	85.2
Quinoid oxygen in ox. prod.,[a] %	17.53	8.94	7.61
m-Dihalogeno-*p*-quinone in ox. prod., %	97.1–97.4	70.5–79.6	84.6–86.9

[a] Average of four or five determinations.

stirring into 200 cc. of water. The crude oxidation product which separated was filtered by suction within one half hour, and dried in a desiccator over concentrated sulfuric acid for about eighteen hours. The experimental data are given in Table I.

Summary

1. The oxidation of *sym*-triiodophenol results in the formation of mononuclear quinone, dinuclear quinone of the cedriret type, chromopolydihalogenophenylene oxide (Lautemann's Red) and an unstable compound which has not been isolated.

2. 2,6,2′,6′-Tetraiododiphenol and 2,6,2′,6′-tetraiododiphenoquinone have been isolated for the first time.

3. The crude oxidation product formed in the oxidation of *sym*-triiodophenol in glacial acetic acid by an excess of chromium trioxide is poorer in mononuclear quinone than that obtained under the same conditions by the oxidation of *sym*-trichlorophenol.

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